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MEMORANDUM



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EXPLORING THE CELL:  
SODIUM  $\beta$ -ALUMINA | CUPRIC CHLORIDE -  
ALUMINUM CHLORIDE - SODIUM CHLORIDE  
BETWEEN 136° AND 200° C

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# EXPLORING THE CELL: SODIUM | $\beta$ -ALUMINA | CUPRIC CHLORIDE - ALUMINUM CHLORIDE - SODIUM CHLORIDE BETWEEN 136<sup>0</sup> AND 200<sup>0</sup> C

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## SUMMARY

Experiments were done with a molten-salt catholyte (initially  $\text{CuCl}_2$  in  $\text{AlCl}_3$ - $\text{NaCl}$ ) separated from molten sodium by  $\beta$ -alumina. The open-circuit reduction potentials were 4.3 and 3 volts for  $\text{Cu}^{++}$  and  $\text{Cu}^+$ , respectively. High polarization and nonrechargeability characterized the cell's operation. The cell's ohmic resistance during discharge was higher than what would be expected from only the ionic resistance of the  $\beta$ -alumina; however, this resistance could be reduced temporarily by a brief period of forced discharge. This cell as constituted is not a practical system.

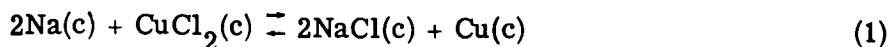
## INTRODUCTION

In the field of high-energy-density cells today, much attention is given to the sodium-sulfur system. In cells of this type the anodic and cathodic materials are, of necessity, very reactive with each other but they must not react except by electrochemical means. A good way to get this result is to separate the two reactants by a "non-permeable" electronically insulating membrane that will conduct an ion needed in the electrochemical reaction. Beta alumina, because it is the best solid conductor of the sodium ion known, has been investigated as a separator in cells that use the molten reactants sodium (Na) and sulfur (S) (e.g., ref. 1, p. 172). The Na|S cell, however, has the disadvantage of operating at a relatively high temperature ( $\sim 350^\circ \text{C}$ ).

The need for high-energy-density cells that will operate at lower temperatures prompted the present work. The intent was to appraise the feasibility of a new catholyte for the Na anode, to make a preliminary electrochemical characterization, and to define problem areas.

The catholyte, initially 0.025-mole-fraction cupric chloride ( $\text{CuCl}_2$ ) dissolved in 2:3 molten sodium chloride ( $\text{NaCl}$ )-aluminum chloride ( $\text{AlCl}_3$ ) was selected for this study

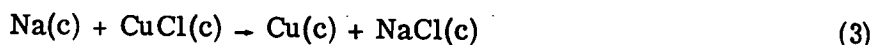
because of its relatively high theoretical power density (for  $\text{Na} \mid \mid \text{CuCl}_2$  per se) of 930 W-hr/kg (420 W-hr/lb), based on the following overall reaction at 25° C:



Open-circuit potentials should be high, 3.6 and 2.7 volts, respectively, based on JANAF free energies in the following reactions at 25° C:



and



Furthermore, the  $\text{Cu}^{++} \mid \text{Cu}^+$  and  $\text{Cu}^+ \mid \text{Cu}^0$  couples are known to be reversible in certain solvents.

A hermetically sealed borosilicate apparatus with tungsten current collectors was used. Measurements were made of open-circuit potentials, currents as a function of potential (during discharge and attempted recharge at various conditions), and instantaneous potential drop during discharge-current interruption. Finally, the  $\beta$ -alumina disk was examined by optical and scanning electron microscopy.

## EXPERIMENTAL PROCEDURE

### Apparatus

A sketch of the experimental cell, which was made of borosilicate glass, is shown in figure 1. Sodium, initially about 1 gram, was placed on top of a high-density  $\beta$ -alumina disk (12 mm diam; 1 mm thick) which, through graded glass, was sealed across the end of a tube. (The  $\beta$ -alumina disk was prepared by the General Electric Research Laboratory and was furnished already sealed to the glass tube.) In the assembly, the disk was submerged about 4 millimeters into the catholyte melt. The catholyte melt was anhydrous purified  $\text{NaCl-AlCl}_3$  (at a 2:3 molecular ratio) and initially contained 0.025-mole-fraction  $\text{CuCl}_2$ . Tungsten (W) wire and foil were used as the two current collectors. Also included in the cell was an Al reference electrode inside a tube of borosilicate glass containing a melt of 2:3  $\text{NaCl-AlCl}_3$  (sans  $\text{CuCl}_2$ ). At 150° C the ionic conductivity of borosilicate glass is high enough for the potential difference between the reference and the working electrodes to be measured by an electrometer.

## Procedure

The reagents were weighed and initially introduced as solids at room temperature into the glass apparatus (through large-bore, vacuum-grade stopcocks) while it was inside a glove box containing a high-purity argon atmosphere. The stopcocks were closed and the apparatus was then removed from the glove box.

The cell was placed in a small oven and its temperature was maintained at  $150^{\circ} \pm 5^{\circ}$  C for most of the experiments. Late in the program, other mean temperatures between  $136^{\circ}$  and  $200^{\circ}$  C were also used. (Both Na and the catholyte are liquids in this range.) Although all reagents were specially purified and dried, the  $\text{NaCl-AlCl}_3$  melt was straw colored. With dissolved  $\text{CuCl}_2$ , the melt was dark brown and nearly opaque.

At various times during the charge life of the cell, open-circuit potentials were measured by an electrometer across the cell and between each working electrode and the Al reference.

Discharge and recharge currents were measured at various cell potentials by a commercial potentiostat. (A minute or so was allowed for stabilization.) These measurements were made (1) for the  $\text{Cu}^{++} \rightarrow \text{Cu}^+$  cathodic reaction (at  $150^{\circ}$  C) 1, 2, and 7 days after initial heatup of the cell and (2) for the  $\text{Cu}^+ \rightarrow \text{Cu}^0$  reaction at  $136^{\circ}$ ,  $163^{\circ}$ , and  $200^{\circ}$  C after the cell had been cooled and reheated.

Resistance of the cell was determined by two methods: (1) from the instantaneous change of potential (measured on a cathode-ray oscilloscope) caused by the interruption of a self-discharging current across a precision resistor (by a mercury-wetted relay) and (2) from plots of  $I$  against  $E$  during discharge. At higher currents (e. g., 10 to 60 mA), the  $\Delta E/\Delta I$  ratio becomes essentially constant and was used to compute resistance.

After the discharge was virtually complete, the cell was disassembled and the parts were examined. The composition of the molten-salt catholyte was checked by chemical analysis, and that of the residue by emission spectroscopy. The  $\beta$ -alumina disk was examined by both optical and scanning electron microscopy.

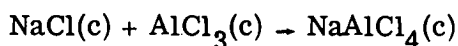
## RESULTS AND DISCUSSION

### Open-Circuit Potentials

Open-circuit potentials between the two working electrodes and between each of these and the Al reference electrode are shown in table I. The data for  $\text{Cu}^{++}|\text{Cu}^+$  against Na were obtained before appreciable  $\text{CuCl}_2$  had been reduced. The open-circuit potential for this cell was greater than 4 volts. Our value for the potential of  $\text{Cu}^{++}|\text{Cu}^+$  against Al, 1.83 volts (table I), is similar to the 1.872 volts (in  $\text{AlCl}_3$ ) obtained in NASA-

sponsored research (ref. 2, p. 163). The  $\text{Cu}^+|\text{Cu}^0$  open-circuit potentials were measured shortly after all  $\text{CuCl}_2$  had been reduced to  $\text{CuCl}$  (as indicated by the absence of intense brown color in the melt). With Na, the potential of the partially reduced catholyte ( $\text{CuCl}$ ) is still desirably high, nearly 3 volts. Our value for the potential (0.74 V) measured against Al is in reasonable agreement with the 0.613 volt reported in reference 2 (p. 137) for  $\text{CuCl}|\text{Cu}$  in  $\text{AlCl}_3$ . Finally, open-circuit potentials of about 1.4 and 1.1 volts for the  $\text{Cu}^{++}|\text{Cu}^+||\text{Cu}^0|\text{Cu}^+$  cell in molten  $\text{NaCl-AlCl}_3$  were calculated (by difference) from the respective Na and Al electrode potentials (table I). These values bracket the value 1.26 computed (table I) from the Al electrode potentials of reference 2.

The measured open-circuit cell potentials (table I) are higher than were computed from thermodynamic data and reactions (2) and (3). The reaction



would add 0.2 volt to the open-circuit potential in each case and can account for the measured cell potential (2.9 V) for the cathodic reaction  $\text{Cu}^+|\text{Cu}^0$  (reaction 3). However, the measured 4.3 volts for the  $\text{Cu}^{++}|\text{Cu}^+$  cathode is still somewhat higher than 3.8 volts (3.6 V (reaction 2) + 0.2 V).

### Operational Behavior

Steady state behavior. - Discharge and recharge behavior of the  $\text{Na}|\text{CuCl}_2$  cell for the first 7 days after initial heatup is shown in figure 2, where current is plotted against the total potential across the cell. The color of the melt suggested that the catholyte reaction was  $\text{Cu}^{++} \rightarrow \text{Cu}^+$ . Several important trends were noted at this time: First, the cell was essentially nonrechargeable, as is shown by the minimal currents at potentials above about 4 volts, which is the initial open-circuit potential. Second, considerable cell polarization occurred during discharge. Third, the Na did not seem to wet the  $\beta$ -alumina initially, and a decrease in polarization on the second day (fig. 2) is thought to result from better wetting. (The lower performance on the seventh day probably results from local depletion of  $\text{Cu}^{++}$  near the  $\beta$ -alumina toward the end of the discharge runs.) Fourth, the cell's ohmic resistance appeared to be fairly independent at lower currents (3 to 60 mA), with respect to the oxidation state of Cu and to the cooling down and reheating of the cell at temperatures as high as  $200^\circ\text{C}$ . Fifth, raising the discharge current to 80 mA and higher reduced the cell resistance by roughly one-half (dashed line - 2nd day). This reduction in cell resistance persisted for a few days even at lower currents, but then the resistance returned to its initial value after several days at open circuit (5 days in this case).

This tendency for the resistances  $R$  to decrease after a discharge of approximately

100 mA and to increase again after several days is illustrated further by resistances measured by the current-interruption method (table II). The last column shows the cell's ohmic resistances at discharge currents of practical interest (3 to 60 mA). Two time intervals are indicated. Total time is given merely as a reference and is the total elapsed days after the first heatup of the cell. The time of present interest is the number of days after discharge at about 100 mA. For the  $\text{Cu}^{++}|\text{Cu}^+$  couple 1 day after the 100-mA discharge, resistance (initially 70 ohms) was reduced to 45 and 41 ohms as measured by the current-interruption method at 16 and 29 mA. As figure 2 shows, the resistance increased again to 72 ohms (at ~10 to 60 mA) 5 days after the 100-mA discharge. Eight days after the 100-mA discharge, a resistance of 74 ohms was shown in one of two current-interruption experiments in the  $\text{Cu}^+|\text{Cu}^0$  catholyte, and after 29 days the resistance was consistently between 64 and 82 ohms. After the second heatup, the resistance was again low (27 to 37 ohms) 4 days after the cell had been discharged at approximately 100 mA. These results indicate that discharge at about 100 mA is an important cell parameter in that it affects significantly the cell's ohmic resistance.

Transient behavior. - The steady conditions shown in figure 2 occurred after several minutes of discharge. After the cell had stood at open circuit for about 1 hour, the discharge current was initially less than that indicated in figure 2. Furthermore, if the cell potential was cycled between 1.8 and 6.7 volts overall by a triangular wave at 0.8 volt per second, the currents at recharge were still similar to those obtained at steady-state potentials (fig. 2). However, the discharge currents during cycling were much more polarized than during use of steady-state potentials and approached the low currents obtained for recharge.

Temperature effects. - The Na|CuCl cell's overall activation energy was estimated from potential-current (E-I) curves at temperatures of 136°, 163°, and 200° C. An example plot of log I against E (in this case at 200° C) is shown in figure 3. The currents at a given potential were smaller when measured during a stepwise increase in current than when measured during a stepwise decrease. Thus, two sets of data result. Each set, in turn, gives rise to two values of the current intercept at rest potential  $I_0$ , one from upward and one from downward extrapolations of I to  $E_0$ . The resultant four  $I_0$  values are shown in figure 3 for increasing and decreasing currents. Each current change gives two slopes - resulting in both an initial and upper limit. Arrhenius-type plots of the four  $I_0$  values at three temperatures are shown in figure 4. The indicated activation energy  $E^*(I_0)$  was roughly 40 kJ/mole (10 kcal/mole). The  $E^*$  for ionic conductivity of  $\beta$ -alumina (single crystal) should be close to 16 kJ/mole (3.8 kcal/mole) (ref. 1, p. 166). Thus, the limiting process in the cell discharge does not seem to be the ion conductivity in the separator. The cell resistances measured in this work also are higher than would be expected from the  $\beta$ -alumina disk.

Polarization. - In the discharge range of possible useful potentials, data from the

current-interruption determinations can be used to yield nonohmic polarizations (by subtracting the instantaneous  $I \cdot R$  drop from the steady-state cell potential). Figure 5 shows cell polarization potential as a function of current (on a log scale). This polarization trend was not affected significantly (1) by the state of Cu oxidation, (2) by time (a total of 96 days standby and downtime), or (3) by shutdown and restart. The slope (roughly 2 V/decade of current) is an order of magnitude higher than Tafel slopes that are due to simple electron-exchange-limited reactions.

### Cell Condition After Discharge

After the cell discharge was virtually complete, the cell was visually inspected, dismantled, and examined in detail. A dark moss and sludge had formed on the W cathodic current collector. Arc emission spectroscopy showed this deposit to be Cu with traces of some other elements.

Both faces of the  $\beta$ -alumina disk were examined with a low-powered binocular microscope, which showed arc-shaped spots on the catholyte side. These spots were variable in size and in a concentration of about 20 per  $\text{cm}^2$ . They consisted of reddish lines on yellowish crescents. One spot was larger than the others, and opposite to it on the Na anode side was a similar-size deposit of amorphous grey material. We conjecture that most of the conduction of  $\text{Na}^+$  occurred at these spots, the residue perhaps being silicates "filtered" from the molten Na. Examination through the binocular microscope gave the impression that the arc-shaped spots occurred at small convolutions or overfolds on the  $\beta$ -alumina surface. This suggests localizations of greater ionic conductivity.

Surprisingly, examination by scanning electron microscopy did not reveal changes in surface composition corresponding to the visible discolorations. In the surface layer characterized by the electron scan, the atomic ratio of Na to Al was only 0.03, which was much less than in the bulk of the ceramic. The lack of Na at the surface was not surprising, because after the glassware was dismantled, the disk had been washed and stored in absolute ethanol. Silicon was also found on the disk; and traces of Cu occurred in some areas (but not coincident with the arc-shaped spots). Scanning electron micrographs showed a uniformly "felted" surface which was characterless with respect to the visible spots.

### SUMMARY OF RESULTS

Experiments with the catholytes  $\text{CuCl}_2$  and  $\text{CuCl}$ , respectively, in molten 2:3  $\text{NaCl-AlCl}_3$  which was separated by  $\beta$ -alumina from a molten Na anode gave the following results:



1. The systems  $\text{Na} || \text{CuCl}_2$  and  $\text{Na} || \text{CuCl}$  behaved as primary cells, at least for limited times.
2. Desirably high, single-cell, open-circuit potentials of 4 and 3 volts, respectively, were demonstrated.
3. The cell was not rechargeable, at least as it was constituted in these experiments.
4. Considerable polarization occurred during discharge and did not seem to be affected by cell age or oxidation state.
5. Ohmic resistance was high but could be reduced by one-half for a short time ( $\sim 5$  days) by a few minutes of forced discharge at 80 to 100  $\text{mA}/\text{cm}^2$  of separator area. This reduced resistance increased again when the heated cell stood for several more days at open circuit.
6. Cell resistance and activation energy indicated that the overall limiting process was not ionic conduction in the  $\beta$ -alumina.
7. Visual evidence suggested that ionic conduction in the  $\beta$ -alumina occurred in localized areas.

## CONCLUSION

Because of its nonrechargeability and its high resistance and polarization during discharge, this cell as constituted is not a practical system.

Lewis Research Center,  
National Aeronautics and Space Administration,  
Cleveland, Ohio, March 18, 1975,  
506-23.

## REFERENCES

1. Kummer, J. T.:  $\beta$ -Alumina Electrolytes. Prog. Solid State Chem., vol. 7, 1972, pp. 141-175.
2. Topol, Leo E.; McCollum, William A., Jr.; and Yosim, Samuel J.: Voltammetric Screening in Fused Salt Electrolytes. (Rept. AI-70-46, North American Rockwell Corp.; NAS3-12970.), NASA CR-72791, 1970.

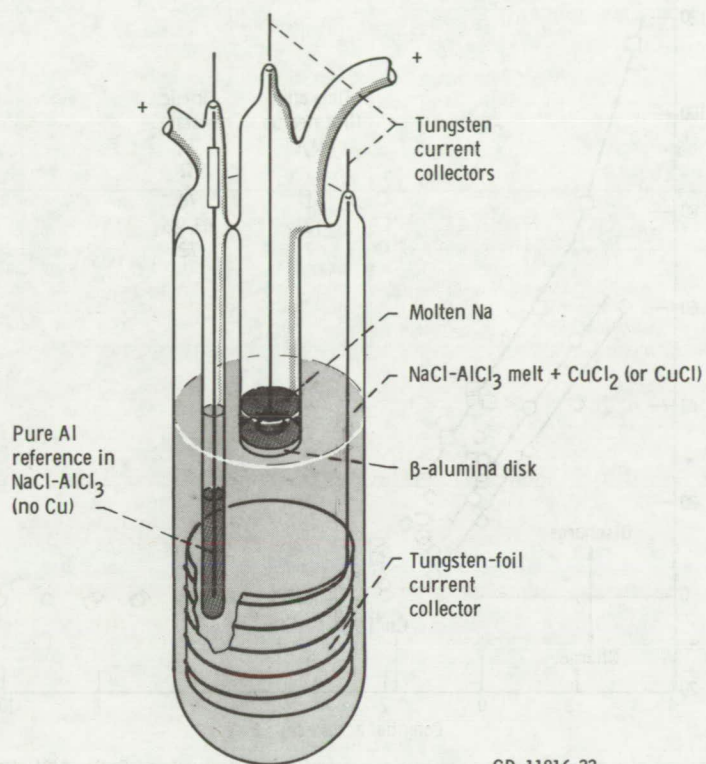
TABLE I. - OPEN-CIRCUIT POTENTIALS

| Postulated system  | This work                                    | In $\text{AlCl}_3$ (ref. 2) |
|--|--|-----------------------------|
|  | Experimental rest potential,<br>$E_0$ ,<br>V |                             |
| From Na anode:   |  |                             |
| $\text{Cu}^{++}   \text{Cu}^+(W)    \text{Na}   \text{Na}^+$                 | 4.30   | -----                       |
| $\text{Cu}^+   \text{Cu}^0(W)    \text{Na}   \text{Na}^+$                    | 2.92   | -----                       |
| $\text{Cu}^{++}   \text{Cu}^+   \text{Cu}^0   \text{Cu}^+$ (dif-<br>ference) | 1.38   | -----                       |
| From Al reference:   |  |                             |
| $\text{Cu}^{++}   \text{Cu}^+   \text{Al}^0   \text{Al}^{+++}$               | 1.83   | 1.872                       |
| $\text{Cu}^+   \text{Cu}^0   \text{Al}^0   \text{Al}^{+++}$                  | .74  | .613                        |
| $\text{Cu}^{++}   \text{Cu}^+   \text{Cu}^0   \text{Cu}^+$ (dif-<br>ference) | 1.09   | 1.259                       |

TABLE II. - OHMIC RESISTANCE OF CELL DISCHARGE  
AT 150° C AS DETERMINED BY CURRENT INTERRUPTION

| Catholyte<br>reaction                    | Total<br>elapsed<br>time,<br>days | Time after<br>~100-mA<br>discharge,<br>days | Current,<br>I,<br>mA | Resistance,<br>R,<br>$\Omega$ |
|--|-----------------------------------|---|----------------------|-------------------------------|
| First heatup                             |                                   |   |                      |                               |
| $\text{Cu}^{++} \rightarrow \text{Cu}^+$ | 1                                 | -1  | ~10 - 60             | <sup>a</sup> 70               |
|  | 3                                 | 1   | 16                   | 45                            |
|  |                                   |   | 29                   | 41                            |
|  | 7                                 | 5   | ~10 - 60             | <sup>a</sup> 72               |
| $\text{Cu}^+ \rightarrow \text{Cu}^0$    | 10                                | 8   | 9                    | 29                            |
|  |                                   |   | 15                   | 74                            |
|  | 31                                | 29  | 8                    | 77                            |
|  |                                   |   | 9                    | 82                            |
|  |                                   |   | 14                   | 64                            |
|  |                                   |   | 14                   | 75                            |
| Second heatup                            |                                   |   |                      |                               |
| $\text{Cu}^+ \rightarrow \text{Cu}^0$    | 96                                | 4   | 3                    | 34                            |
|  |                                   |   | 10                   | 37                            |
|  |                                   |   | 19                   | 27                            |

<sup>a</sup>From limiting  $\Delta E/\Delta I$  (fig. 2).



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Figure 1. - Arrangement of cell.

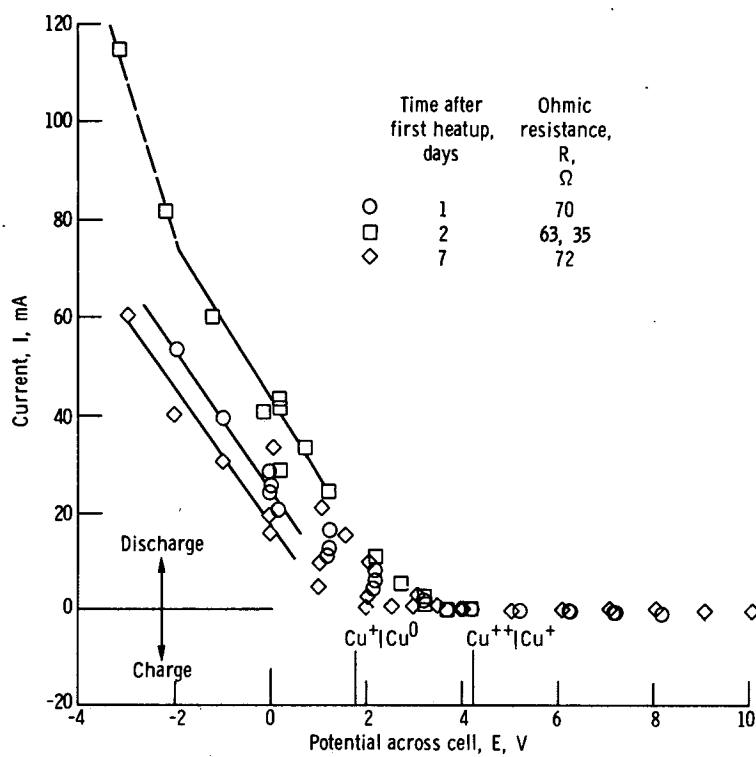


Figure 2. - Steady-state discharge and recharge of Na |  $\beta$ -alumina |  $\text{CuCl}_2\text{-AlCl}_3\text{-NaCl}_2$  cell at 150°.

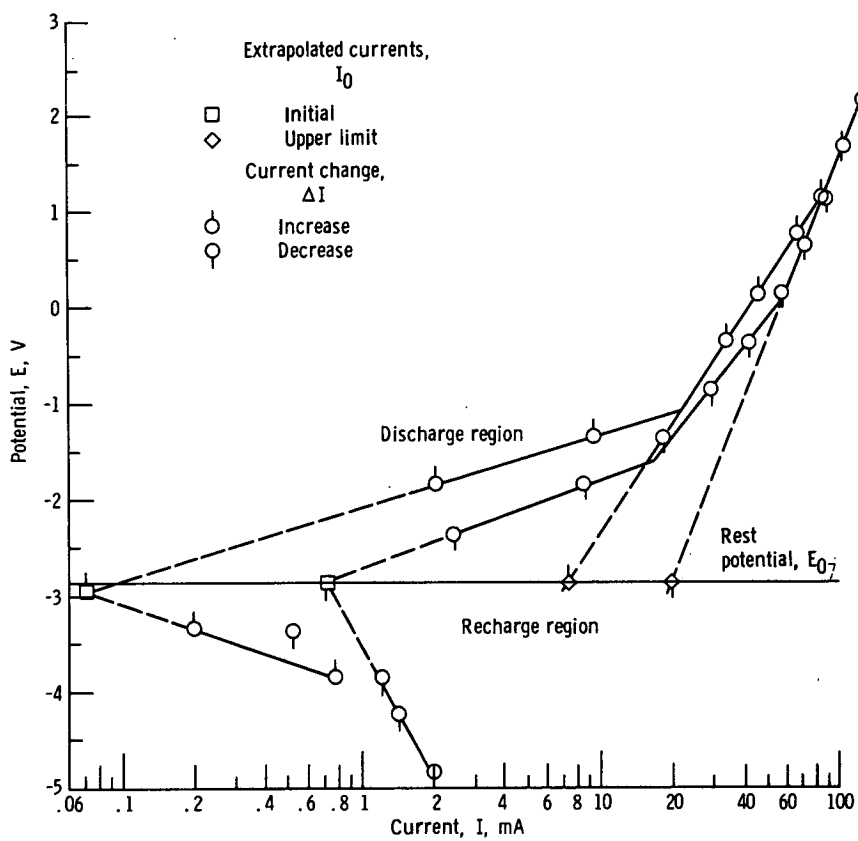


Figure 3. - Performance of Na || CuCl cell at 200°C.

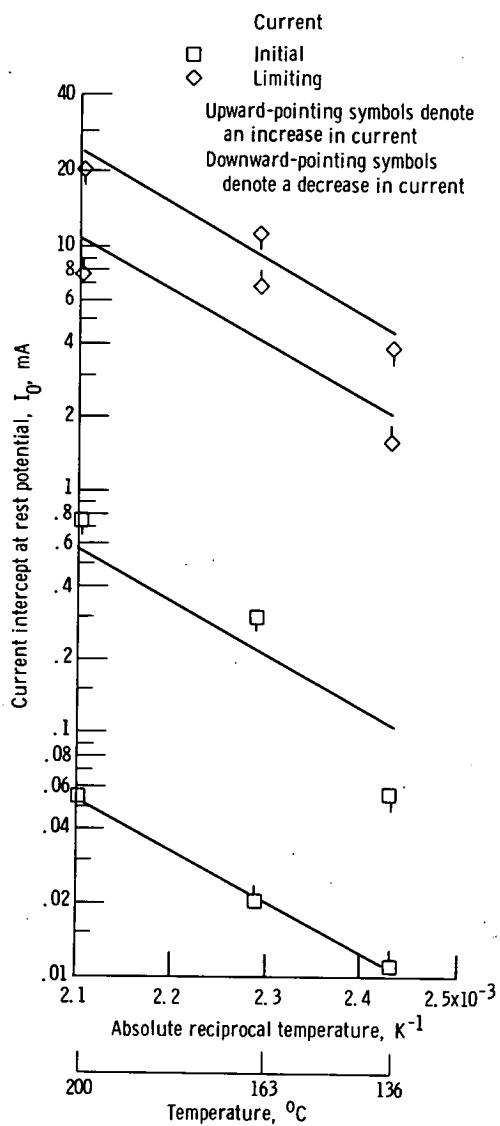


Figure 4. - Arrhenius-type plot of current intercepts.

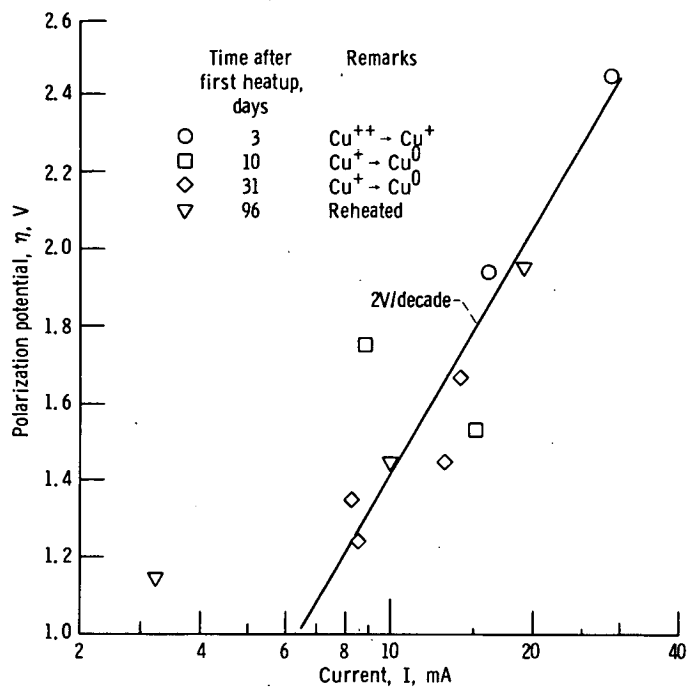


Figure 5. - Polarization of cell.

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